

Thermodynamics of the λ -transition in superconductors

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With 7 figures in the text

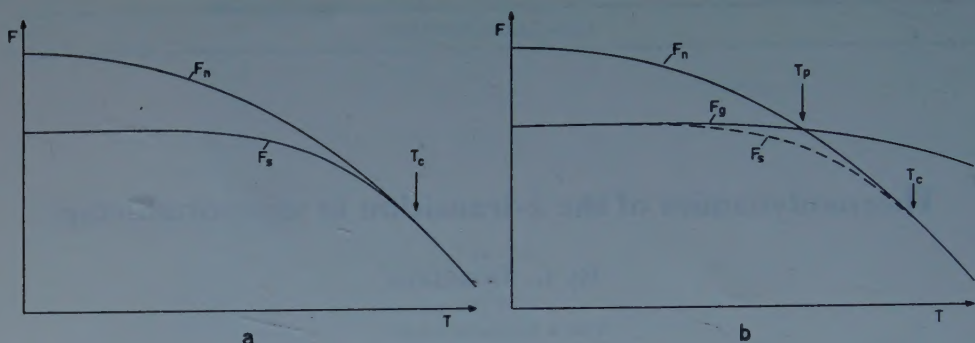
1. Introduction

From the point of view of electric conductivity, the transition in superconducting metals appeared rather discontinuous with a sharp break at the critical temperature T_c . Twenty years after the discovery of the superconductivity by Kamerlingh Onnes the colorimetric measurements of Keesom and his collaborators showed, however, that the transition was of the type now called λ -transition with a continuous change of the energy content but a rather sharp change of its derivative, the specific heat, at or very near T_c .

For the mathematical description of the variations of the energy content in λ -transitions as a function of temperature two different ways have been tried, both based on general thermodynamics. They are illustrated in fig. 1 by the diagrams a and b of the free energy F as a function of the Kelvin temperature T .

In the procedure illustrated by fig. 1 a two states of the substance are considered. One of these has the lower free energy and is the stable one below the critical point T_c . At T_c the free energy curve of this state joins that of the other state without a break in the derivative which is the thermodynamic condition for a second order transition. The possibility of a formal treatment of λ -transitions in this way was observed by Ehrenfest in 1933. It is obvious, however, that such a smooth contact of the free energy curves of two different phases cannot be expected to occur repeatedly in nature just by chance. There must be a physical reason for the two curves to approach in this special way with an increasing temperature. The central problem is therefore to describe mathematically the free energy curve below T_c in a way that agrees with calorimetric data and at the same time hints at a physical interpretation. The earlier thermodynamic studies of the λ -transitions in superconductors by Gorter and Casimir [1], Ginsburg [2], Koppe [3], Bender and Gorter [4], Marcus and Maxwell [5], Corak, Goodman, Satterthwaite and Wexler [6], are all along this line.

The other way to look at the λ -transitions, illustrated by fig. 1 b, is to start from a consideration of the free energy of two relatively simple limiting states, the one approached at a very low temperature and the other stable above the critical point. If no intermediate states were possible the free energy curves should intersect and there should be a discontinuous phase transition of the first order at a temperature T_p lower than T_c . The reason for a continuous transition is the possibility of a continuous series of intermediate states, with free energies lower

Fig. 1. Free energy-temperature diagrams for λ -transitions.

than those of any of the limiting states, in a range of temperature on both sides of T_p . The free energy of the stable states in this range (the dashed line in fig. 1 b) is the envelope of theoretical curves describing free energy as a function of temperature for a continuous series of intermediate structures.

This way of looking at the λ -transitions was introduced by the present writer and his collaborators [7] already in 1928 in connection with the first studies of the order-disorder transformations in alloys. These transformations are mainly determined by the structural energy E_{str} , structural entropy S_{str} and structural free energy

$$F_{\text{str}} = E_{\text{str}} - T S_{\text{str}} \quad (1)$$

of the intermediate states between full order and full disorder [8] while the changes in thermal energy and entropy due to lattice vibrations seem to be relatively small. The various types of order-disorder transition are dependent on the relationships between E_{str} and S_{str} [9]. These relationships are rather complicated and a number of different theories vary in the way they try to combine E_{str} and S_{str} often as functions of some special parameter of order or disorder.

The λ -transitions in superconductors to be discussed in the following as well as the transition in liquid helium which was recently discussed in an analogous way [10] are in one respect more complicated than the order-disorder transformations in alloys as not only structural but also thermal energy is changed by the transition. On the other hand in the low-temperature transitions there seem to be only two possible states for the conducting electrons or the atoms. They belong either to the ground state or to excited groups of atoms, while in the alloys there is a variety of structural configurations.

2. Procedure of the thermodynamic analysis

Adopting the second way of treatment outlined above we consider three different states of a superconducting metal. 1:0 the state which is approached near the absolute zero point with no excitations other than the phonons of the lattice vibrations. We shall call this the superconducting ground state or simply the ground state. 2:0 the state of transition below the critical point T_c . In the tra-

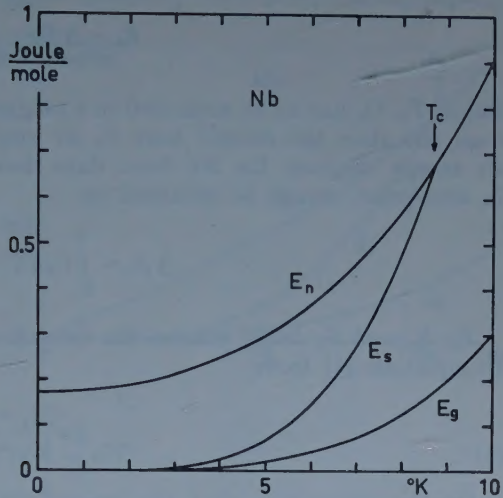


Fig. 2. Energy-temperature diagram for niobium.

ditional way we shall call this the superconducting state. 3:0 the normal state stable above T_c in a zero magnetic field and also below T_c in an applied field.

If we choose the ground state at $T=0$ as zero point of our energy scale, the energy pro mole of the ground state is that of the lattice vibrations. In zero magnetic field it is a function of T only.

$$E_g = E_g(T) \quad (2)$$

The energy of the normal state is

$$E_n = E_g(T) + \Delta E_z + \frac{\gamma}{2} T^2 \quad (3)$$

where ΔE_z is the difference in zero-point energy between the normal state and the ground state at a zero magnetic field, and $\gamma T^2/2$ the thermal energy of the electrons in the normal state. If there are only two energy states of the atoms, the energy of a state of transition with a fraction $1-x$ of the atoms belonging to the ground state and x atoms to the normal state, is

$$E_s = (1-x) E_g + x E_n = E_g(T) + x \Delta E_z + x \frac{\gamma}{2} T^2 \quad (4)$$

The energy in the superconducting state of transition is obtained experimentally from the atomic heat C_s measured at a zero magnetic field as

$$E_s = \int_0^T C_s dT \quad (5)$$

The thermal part of the energy of the normal state is obtained from the atomic heat C_n of this state by integration. The total E_n is

$$E_n = \Delta E_z + \int_0^T C_n dT \quad (6)$$

Below T_c , C_n has to be measured in a magnetic field, which as found experimentally does not alter the atomic heat C_n as long as the field is constant. Fig. 2 shows an energy diagram for Nb from data derived in the next section. The difference in zero-point energy is obtained as

$$\Delta E_z = \int_0^T C_s dT - \int_0^T C_n dT \quad (7)$$

E_s , E_n and E_g being known the transition parameter x is obtained, according to equation (4) from

$$x = \frac{E_s - E_g}{E_n - E_g} \quad (8)$$

On the assumption that the ground state and the normal state are both states of equilibrium with zero entropy at $T=0$ the entropy of the ground-state is that of the lattice vibrations

$$S_g = S_g(T) \quad (9)$$

and the entropy of the normal state is

$$S_n = S_g(T) + \gamma T \quad (10)$$

γT being the entropy of the electrons. The entropy of the intermediate superconducting state S_s is assumed to be the sum of a thermal part $(1-x)S_g + xS_n$ and a structural part $\Delta S_m(x)$ due to a mixing of the two states, that is

$$S_s = S_g(T) + x\gamma T + \Delta S_m(x) \quad (11)$$

Our main purpose is the determination of $\Delta S_m(x)$ which as found from the equations (9), (10), and (11) is

$$\Delta S_m = S_s - S_g - x(S_n - S_g) \quad (12)$$

S_s and S_n are determined from the measurements of the atomic heats C_s and C_n by integrating as

$$S_s = \int_0^T \frac{C_s}{T} dT \quad (13)$$

and

$$S_n = \int_0^T \frac{C_n}{T} dT \quad (14)$$

At the critical point T_c where the two states coincide we should, if our assumption that they are both states of equilibrium is right, have

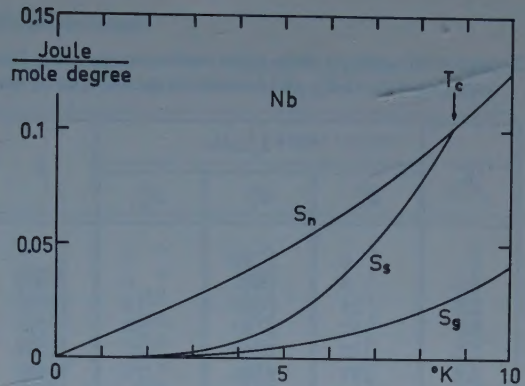


Fig. 3. Entropy-temperature diagram for niobium.

$$\int_0^{T_c} \frac{C_s}{T} dT = \int_0^{T_c} \frac{C_n}{T} dT \quad (15)$$

This condition is fulfilled within the limits of errors for all superconductors for which suitable calorimetric data are available.

Fig. 3 shows the entropy diagram for Nb.

3. Niobium

Nb has been extensively investigated by Brown, Zemansky and Boorse [11]. From their measurements of the specific heat C_s in the superconducting state we have according to the expressions (5) and (13) determined the value of E_s and S_s in Table 1 by graphical integration. The specific heat C_n in the normal state had been found to obey an expression which, using Joule/mole degree as units, gives

$$C_n = 1.215 \times 10^{-4} T^3 + 85.4 \times 10^{-4} T \text{ J/mole degree} \quad (16)$$

The first term refers to the lattice vibrations. Because of the rather high Debye temperature, 252 °K, the T^3 -law is valid with sufficient accuracy up to the critical temperature $T_c = 8.7$ °K. The second term in (16) is due to the electron gas. An integration of the first term gives the lattice energy E_g , an integration of this term divided by T gives the lattice entropy S_g . Integration over both terms of C_n and addition of a zero-point energy $E_z = 0.172$ J/mole in order to fulfil the condition (7) gives the values of E_n . Integration of C_n/T gives the entropy S_n of the normal state. The transition parameter x is obtained from E_s , E_n and E_g according to equation (8) and the structural entropy of mixing ΔS_m from S_s , S_n , S_g , and x according to equation (12). The calculated values of x and ΔS_m are seen in the Table. At the critical point $T = 8.7$ °K the derived values of S_s and S_n are very nearly the same in accordance with the thermodynamic condition (15). This supports the accuracy of the measurements.

In figure 4 the entropy of mixing ΔS_m is plotted against x and compared with the expression

Table 1. Niobium.

Energy and entropy data from measurements by Brown *et al.* (11). Calculated values of the zero-point energy ΔE_2 , the transition parameter x , and the structural entropy of mixing ΔS_m .

°K	10 ⁻⁴ J/mole			x	10 ⁻⁴ J/mole degree			
	E_s	E_n	E_g		S_s	S_n	S_g	ΔS_m
0	0	1720	0	0	0	0	0	0
2.0	9	1897	5	0.002	6	174	3	2
2.5	25	2000	12	0.006	12	220	6	5
3.0	57	2130	25	0.016	24	267	11	9
3.5	122	2289	46	0.034	44	316	17	15
4.0	233	2485	78	0.065	73	368	26	25
4.5	408	2711	125	0.109	113	421	37	35
5.0	659	2974	190	0.168	166	478	51	44
5.5	1005	3292	278	0.241	232	537	67	51
6.0	1460	3655	394	0.327	311	600	88	56
6.5	1923	4067	542	0.426	404	666	111	56
7.0	2775	4543	729	0.536	512	737	139	52
7.5	3675	5084	961	0.658	632	807	167	42
8.0	4774	5698	1244	0.792	778	891	207	28
8.5	6095	6391	1585	0.940	938	975	249	7
8.7	6693	6693	1740	1	1007	1010	267	0

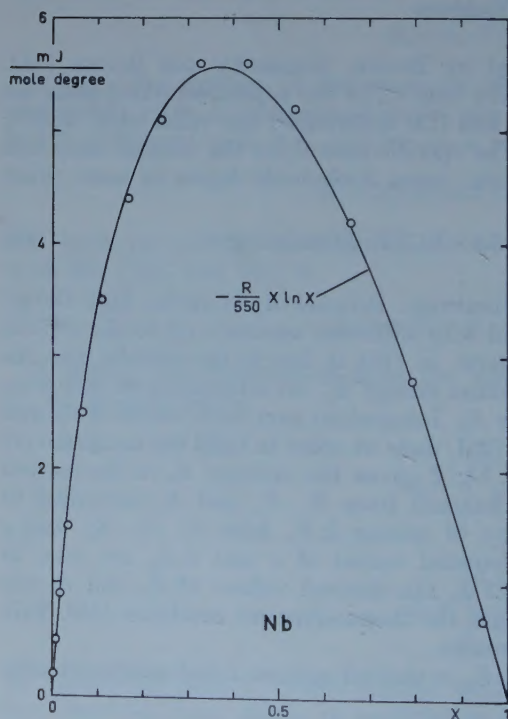


Fig. 4. Structural entropy of mixing ΔS_m versus transition parameter x for niobium.

Table 2. Vanadium.

Energy and entropy data from measurements by Corak *et al.* (12). Calculated values of the zero-point energy ΔE_z , the transition parameter x , and the structural entropy of mixing ΔS_m .

°K	10 ⁻⁴ J/mole			x	10 ⁻⁴ J/mole degree			
	E_s	E_n	E_g		S_s	S_n	S_g	ΔS_m
0	0	569	0	0	0	0	0	0
1.5	6	674	1	0.018	5	140	1	3
2.0	38	756	2	0.048	22	187	1	12
2.5	116	863	5	0.129	56	234	3	24
3.0	260	996	10	0.253	108	282	5	34
3.5	485	1155	19	0.413	178	331	7	37
4.0	806	1342	32	0.591	262	381	11	33
4.5	1237	1558	52	0.786	364	432	15	21
4.97	1757	1790	77	0.980	475	481	21	3
5.06	1837	1837	83	1	491	490	22	0

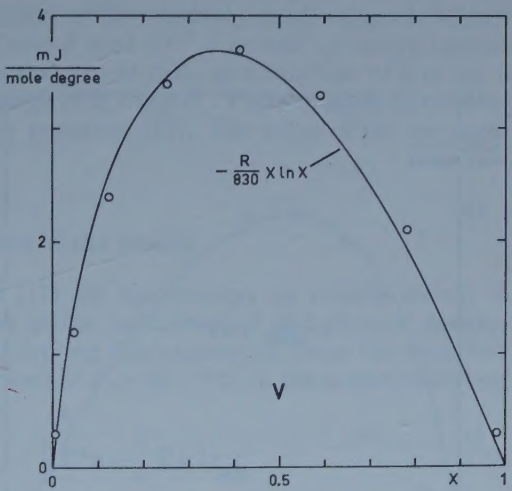


Fig. 5. Structural entropy of mixing ΔS_m versus transition parameter x for vanadium.

$$\Delta S_m = -\frac{R}{n} x \ln x$$

(17)

With the empiric value $n=550$ of the constant the agreement is well within the probable limits of the uncertainty of the experimental results.

4. Vanadium

V has been extensively investigated by Corak, Goodman, Satterthwaite, and Wexler (6) who have given a great number of determined values of C_s and C_n adjusted to a corrected temperature scale. From plots of C_s respectively C_s/T against T we have determined the values of E_s and S_s to be found in Table 2. The results for C_n are given by the formula

Table 3. Tin.

Energy and entropy data from measurements by Corak *et al.* (6). Calculated values of the zero-point energy ΔE_z , the transition parameter x , and the structural entropy of mixing ΔS_m .

°K	10 ⁻⁵ J/mole			x	10 ⁻⁵ J/mole degree			
	E_s	E_n	E_g		S_s	S_n	S_g	ΔS_m
0	0	596	0	0	0	0	0	0
0.5	0	619	1	0.000	1	88	1	0
1.0	13	691	7	0.007	16	183	8	6
1.5	75	829	36	0.049	65	292	29	23
2.0	270	1056	110	0.169	174	420	70	45
2.25	441	1212	173	0.258	255	493	99	54
2.5	669	1402	259	0.359	352	574	136	59
2.75	975	1640	382	0.472	469	664	183	59
3.0	1373	1930	526	0.603	605	765	240	49
3.25	1876	2290	770	0.733	767	880	311	39
3.5	2515	2732	1064	0.870	955	1010	398	24
3.74	3259	3252	1432	1	1158	1153	449	0

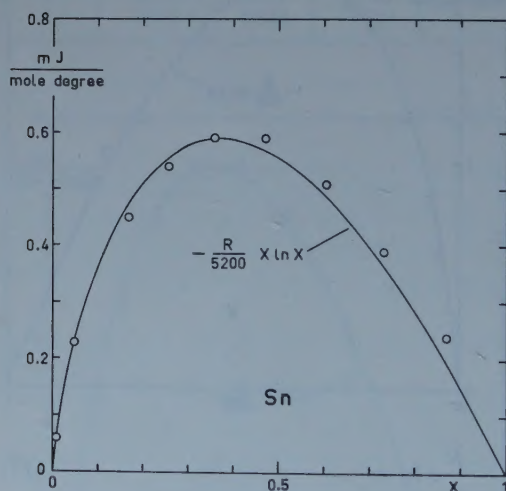


Fig. 6. Structural entropy of mixing ΔS_m versus transition parameter x for tin.

$$C_n = 0.5036 \times 10^{-4} T^3 + 92.6 \times 10^{-4} T \text{ J/mole degree} \quad (18)$$

The Debye θ is found to be 338°K. From these values we have, as described in the case of Nb, determined the tabulated values of E_g , E_n , S_g , and S_n . The zero-point energy ΔE_z is found to be 0.0569 J/mole. Also in this case the agreement of S_s and S_n at the transition point is well established. The transition parameter x is calculated from equation (8) and the structural entropy of mixing ΔS_m from equation (12). As seen from figure 5 ΔS_m as a function of x agrees within reasonable experimental uncertainty with the expression (17) with $n=830$.

5. Tin

Sn has been calorimetrically investigated already by Keesom and his co-workers and recently with greater accuracy by Corak and Satterthwaite [12], which have given extensive tables of primary results for C_s and C_n . From their values of C_s we have obtained the values of E_s and S_s in Table 3 by graphical integration. Below 2.5°K the specific heat C_n of the normal state was found to follow the formula

$$C_n = 2.62 \times 10^{-4} T^3 + 17.5 \times 10^{-4} T \text{ J/mole degree} \quad (19)$$

Above 2.5°K there were, however, deviations from the T^3 law for the part due to lattice vibrations. We therefore have determined E_n and S_n by graphical integration of diagrams of C_n and C_n/T against T . The zero-point energy was found to be $E_z = 596 \cdot 10^{-5}$ Joule/mole. The energy E_g and entropy S_g due to the lattice vibrations are then obtained by subtracting the electron energy $\gamma T^2/2$ from $E_n - \Delta E_z$ and the electron entropy γT from S_n . The transition parameter x and the structural entropy of mixing ΔS_m were determined as in the earlier cases. There is again good coincidence between the entropy values S_s and S_n at the critical point. It has to be observed that because of the relatively small values of energy and entropy in this case we have in Table 3 used 10^{-5} J as unit of energy instead of 10^{-4} J in the Tables 1 and 2. Also the plot of ΔS_m as a function of x in fig. 6 is made on another scale than in the cases of Nb and V. There is again agreement within reasonable limits of error, with equation (17). The value of the empirical constant is found to be $n = 5200$.

6. Discussion of the results

We have arrived at the expression (17) for the entropy of mixing mainly in an empirical way and we shall now look at the mathematical and physical description of the λ -transitions we obtain by adopting this expression. From the equations (4), (10), and (17) we obtain the free energy $F_s = E_s - TS_s$ in the superconducting state as

$$F_s = F_g(T) + \Delta E_z x - \frac{\gamma}{2} T^2 x + \frac{R}{n} T x \ln x \quad (20)$$

This formula contains, as do several formulae proposed earlier three constants. They are put together in Table 4. The combination of the two variables T and x is, however, a new one and the new constant n indicates a new physical interpretation.

The condition for equilibrium at a certain temperature T is

$$\frac{\partial F_s}{\partial x} = \Delta E_z - \frac{\gamma}{2} T^2 + \frac{R}{n} T (1 + \ln x) = 0 \quad (21)$$

For $n = \infty$ the entropy of mixing should disappear. At a temperature of

$$T_p = \sqrt{\frac{2 \Delta E_z}{\gamma}} \quad (22)$$

Table 4. Empirical constants for superconductors and liquid helium.

	$\frac{\Delta E_z}{\text{J/mole}}$	$\frac{\gamma}{\text{J/mole. deg}^2}$	n	T_p °K	T_c °K	α
Sn	0.00596	0.00175	5 200	2.61	3.71	1.43
V	0.0569	0.00926	830	3.51	4.97	1.62
Nb	0.172	0.00854	550	6.35	8.70	1.79
He	5.5	3.14	8.5	1.87	2.17	3.0

we should then get an ordinary discontinuous transition. T_p is the temperature where the free energy curves for the ground state and the normal state intersect in the diagram of fig. 1 b, which quantitatively corresponds to the case of niobium if the line drawn along the ordinate axis corresponds to 0.65 J/mole degree and that along the absciss axis to 10°K. The values of T_p are given in Table 4 together with the critical temperatures T_c .

The most obvious interpretation of the expression (17) for the entropy of mixing is that the excited normal state appears in the ground state as macromolecules, or microdrops, each excitation covering, perhaps as a mean, n atoms. This picture is supported by the fact that the smallest quantity of energy necessary to form such a microdrop $n\Delta E_z/N$, where N is the number of atoms in a mole, is of the same order as the average excitation energy at the transition point, the product kT_p , where k is the Boltzmann constant. The ratios

$$\alpha = \frac{n\Delta E_z}{NkT_p} = \frac{n\Delta E_z}{RT_p} \quad (23)$$

for the three superconductors examined, shown in Table 4, have values between 1.4 and 1.8.

Introducing the dimensionless quantity α and corresponding temperatures T/T_p in the equation (21) we obtain after a simple transformation the equilibrium condition in the form

$$x = \exp \left[\alpha \left(\frac{T}{T_p} - \frac{T_p}{T} \right) - 1 \right] \quad (24)$$

with just two parameters α and T_p characteristic of the metal in question. We observe that this simple form is dependent on the use of the phase-transition temperature T_p and not, as in some earlier theoretical treatments, of the critical temperature T_c as reference temperature. Fig. 7 illustrates the dependence of x on T/T_p for the α -values 1, 2, 3, and ∞ .

The present treatment of the superconductors is analogous to the author's recent treatment of the λ -transition in liquid helium [10]. For comparison the values of ΔE_z , γ and n from that paper and computed values for T_p and α are introduced in Table 4. Recent more elaborate measurements of the specific heat above the λ -point by Hill and Lounasmaa [13] give slightly different values. It is interesting

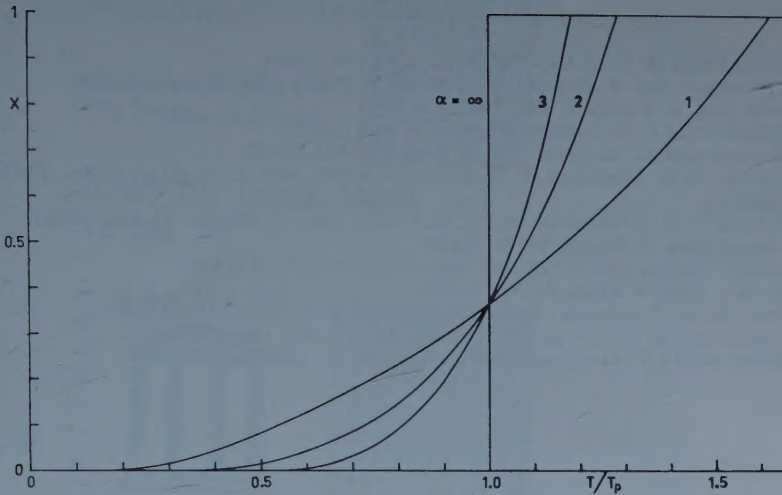


Fig. 7. The transition parameter x as a function of the reduced temperature T/T_p .

to notice that the high value of ΔE_z and the low value of n compensate each other so that α is still of the order of unity. The critical temperatures T_c given in the table correspond to the maxima of specific heat. In the superconductors the anomalies of the specific heat disappear a few hundredths of a degree above these maxima. In liquid helium the anomaly can be traced a full degree above the maximum. These details at the upper end of the transition are not described by equation (24). It is obvious that the theory is in need of further refinement for values of x near to unity.

Our thermodynamic discussion is based on measurements on the superconducting state in a zero magnetic field and on the normal state in constant fields strong enough for its maintenance. This is made possible by the fact that the specific heat of the normal state, including the constant γ , is not appreciably varied by the field. The decreasing of the critical temperature T_c with increasing field strength is obviously mainly due to a decrease in the difference in zero-point energy ΔE_z by a raising of the energy of the highly diamagnetic ground state. There is so far no experimental basis for judging whether the number n is also changed by the magnetic field.

We have no reason to enter here into the separation in a metal specimen of domains of superconducting and normal states by varying magnetic fields. We just observe that this macroscopic separation is entirely different from the formation and resolution of microdrops of molecular dimensions of the normal state in the ground state which we think is occurring in the superconducting regions.

The profound theoretical problem concerning the quantum-mechanical difference between the ground state and the normal state is also outside the scope of the present paper. It may be possible, though, that the determination of the constants n and the idea of excited macromolecules can be of some use in solving this problem.

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